

Appendix C – Quality Assurance Assessment

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**ANALYTICAL CHEMISTRY QUALITY ASSURANCE/QUALITY CONTROL
SAN DIEGO COUNTY OPERATIONS CENTER
POROUS PAVEMENT/TREATMENT TRAIN
2006 - 2008 STORMWATER MONITORING PROJECT**

Kinnetic Laboratories conducts all activities in accordance with formal QA/QC procedures. Quality Assurance and Quality Control (QA/QC) consists of evaluating the field duplicates and laboratory quality control samples for compliance associated with the field sampling and laboratory. Field QA/QC samples are used to evaluate potential contamination and sampling error introduced prior to submittal to the analytical laboratories. Laboratory QA/QC activities provide information needed to assess potential laboratory contamination, analytical precision and representativeness.

The overall QA objective is to ensure that data of known and acceptable quality are provided. The primary indicators used to evaluate the quality of the data are precision, accuracy, representativeness, comparability and completeness. The following sections define each of these indicators and how they are used to assess and validate data from this project.

1.0 QUALITY ASSURANCE/QUALITY CONTROL METHODS

The chemistry records for the 2006 - 2008 San Diego County Operations Center Stormwater Monitoring Project Quality Assurance/Quality Control (QA/QC) were inspected using the EPA documents for organic and inorganic review for guidance and compared to the Phase I and Phase II Project QAPPs and Monitoring Plans (Kinnetic Laboratories, Inc. 2004; MEC-Weston, 2004, Kinnetic Laboratories, Inc. 2007).

The overall quality of the dataset is determined to a large degree by the thoroughness, accuracy and precision of the laboratory QC records, which explains why the majority of this section is devoted to examining them in detail. The QC is tabulated by category and each is discussed individually. Generally the results were well within the appropriate ranges and limits and any significant exceptions and any resulting data qualifications are presented in detail in this section and reflected in the summary tables found in the main body of the document.

1.1 Precision

Precision provides an assessment of mutual agreement between repeated measurements. These measures may apply to blind field duplicates (FD), laboratory duplicates (DUP), matrix spike duplicates (MSD) and laboratory control sample duplicates (LCSD). Monitoring of precision through the process allows for the evaluation of the consistency of field sampling and laboratory analysis.

The Relative Percent Difference (RPD) is used to evaluate duplicate samples. The RPD is the difference between the two samples divided by their average expressed as percent and is calculated as:

where:

$$RPD = 200 * \left(\frac{|x_1 - x_2|}{x_1 + x_2} \right)$$

x_1 = Concentration of sample 1 of the pair
 x_2 = Concentration of sample 2 of the pair

1.2 Accuracy

An assessment of the accuracy of measurements is based on determining the difference between measured values and the known or “true” value and is applied to Matrix Spikes (MS), Laboratory Control Samples (LCS) and Standard Reference Material (SRM).

In general, Percent Recovery is calculated as:

$$\%R = 100 * \left(\frac{\text{Measured_Value}}{\text{True_Value}} \right)$$

Matrix Spike recoveries take into account the concentration of the source sample.

$$\%R_{MS} = 100 * \left(\frac{\text{Measured_Value} - \text{Sample_Value}}{\text{True_Value}} \right)$$

1.3 Representativeness, Comparability and Completeness

Representativeness is the degree to which data accurately and precisely represents the natural environment.

Comparability is the measure of confidence with which one dataset can be compared to another. The use of standardized methods of chemical analysis and field sampling and processing are ways of insuring comparability. The implementation of thorough QA/QC methods such as field duplicates and laboratory QC is essential.

Completeness is a measure of the percentage of the data judged valid after comparison with specific validation criteria. This includes data lost through accidental breakage of sample containers or other activities that result in irreparable loss of samples. Implementation of standardized Chain-of-Custody procedures which track samples as they are transferred between custodians is one method of maintaining a high level of completeness.

A high level of completeness is essential to all phases of this study due to the limited number of samples. Of course, the overall goal is to obtain completeness of one hundred percent however a realistic data quality objective of 95% will insure an adequate level of data return.

Close adherence to ‘Standard Operating Procedures’ (SOP’s) assures that the resulting data is representative, complete and comparable. The results are further assessed with a thorough validation process.

2.0 DATA QUALITY ASSESSMENT PROCESS

2.1 Verification

Data verification was the first step in the data quality assessment process. The verification process generally included checks to verify compliance with the sampling plan and with the QA/QC practices. Information contained in the laboratory reports was verified to be complete, correct and free of inconsistencies.

2.2 Validation

Data validation was performed in accordance with the National Functional Guidelines for Organic Review (EPA 540-R-99-008, October 1999), Low Concentration Organic Review (EPA 540-R-00-006, June 2001) and Inorganic Data Review (EPA 540-R-01-008, July 2002). All laboratory and field data generated under the program were reviewed for accuracy, precision and completeness. The review included:

- Data package completeness
- Chain-of-Custody
- Use of specified analytical methods
- Holding times for extraction and analysis
- Blanking results (equipment, bottle, filter, and method blanks) relative to the reporting limits and sample concentrations
- Field duplicate frequency and precision
- Laboratory duplicates, frequency and precision
- Laboratory Control Sample frequency, compounds and recoveries
- Surrogate standard frequency, compounds and recoveries
- Matrix spike frequency, compounds and recoveries
- Matrix spike duplicate frequency and relative percent differences
- Reporting limits and dilution factors

2.3 Data Qualifiers

Where appropriate, data qualifiers were associated with the results using the following standard notations from the EPA guidance documents

<u>Data Review Qualifiers</u>	
U	The compound was analyzed for but was not detected. The associated value is the sample reporting limit
UJ	The compound was analyzed for but was not detected. The associated value is an estimate and may be inaccurate or imprecise
J-	The associated value is a low estimate
J	The associated value is an estimated quantity
J+	The associated value is a high estimate
R	The data are unusable. The analyte may or may not be present

The EPA guidance documents are clear that data review and qualification rules are to be tempered using professional judgment and the specifics are discussed in the following section of this report.

3.0 PROJECT SPECIFIC CHEMISTRY DATA REVIEW

Nine events were monitored at the San Diego County Operations Center during the project for a total of 55 individual station events, counting the field duplicates.

A detailed review of the chemistry records found only five cases where further qualification was warranted. Those cases are detailed in the following discussion.

3.1 Holding Times

Holding times were met during the 2007 - 2008 project year with two significant exceptions. Nitrate as N and orthophosphate were run 24 hours out of the 48 hour hold time for the last asphalt lysimeter station event and the associated samples were qualified with a J to indicate that they are to be treated as estimates.

3.2 Equipment Blanks

Blanks were analyzed to assess potential contamination from composite bottles and tested for four total metals (Cd, Cu, Pb, Zn) and seven conventional contaminants (DOC, COD, ammonia as N, TKN, nitrate as N, orthophosphate as P, total phosphorus on a per batch basis. Four batches of twenty bottles were cleaned for this project year with one bottle from each serving as the blank for that group. No contaminants were found in any of the blanking studies performed for this study.

In general, if a contaminate is found in an equipment blanking study, all associated samples that have a concentration less than five times the blank hit are qualified with a 'J+' flag. Samples with relatively high concentrations are unaffected. Since no contaminants were present in any of the equipment blanks, none of the samples required qualification.

3.3 Field Duplicates

Sub-sampling splits of the composite samples were taken from the County Operations Center and, while not true field duplicates, are assessed as field duplicates. They indicate that the sub-sampling process was, in most cases, able to effectively obtain representative samples from the composite during the project.

A summary of field duplicate stations and dates is presented in Table C-1. Strict criteria are not established for the evaluation of field duplicates. Rather samples are evaluated based upon best professional judgment. Relative percent differences were highlighted when greater than 50% and were given closer scrutiny. As a general rule, values are considered to be of concern if above 50% provided both values are greater than five times the reporting limit. In cases where one or both values are less than five times the reporting limit those values are considered to be of potential concern if the difference between the two values is greater than twice the reporting limit.

With one exception the RPDs for the composite field duplicates were all either small or associated with small absolute differences and were well within QC guidelines.

The suspended solids concentration (SSC) coarse fraction (>63 micron) from the 7 Dec 2007 event had a field duplicate RPD of 54% with an absolute difference of 13 mg/L. The duplicate was taken at the Phase II parking lot reference site which was observed to receive sediment contamination from the adjacent construction runoff. The SSC variance was not considered representative of all the sites. The SSC coarse fraction was assigned a "J" qualifier for that first event of the 2007/2008 storm season at the COC parking lot reference site but the other sites were unaffected.

4.0 ANALYTICAL CHEMISTRY QA/QC

This section address procedures and errors associated with laboratory handling and analysis. In most cases, the QA/QC results have been summarized for each type of assessment. There were no substantive laboratory issues requiring further qualification of the results.

4.1 Reporting Limits

KLI performed a review of the detection limits reported by the laboratories to ensure that they met the project requirements. All required detection limits were met.

4.2 Method and Filter Blanks

When evaluating laboratory blanks the general rule is: Samples whose values are more than 10 times the blank hit are not affected. Those samples whose values are less than 10 times the blank hit are qualified as J+ to indicate a high bias. Analytes that are not detected at the reporting limit are not affected.

Our review of the results shows that the laboratory blanks for this project were free of significant contamination with two exceptions:

- There was a TKN blank hit of 0.143 mg/L and another of 0.136 mg/L for the batches associated with the first three events. Using the larger of the two values as the guide there were only two cases where the sample values were less than 1.43 mg/L. All other were unaffected. The Media Filter Influent and Effluent sample concentrations were qualified with a J+ to indicate that they should be treated as high estimates.
- The other significant blank hit was 1.56 ug/L for total zinc for the sixth event (7 Dec 2007). The lysimeter results were below 15.6 ug/L qualification limit and were assigned J+ to indicate that they are to be treated as high estimates. All other total zinc values for that event were unaffected.

4.3 Laboratory Replicates

Replicate samples were analyzed to evaluate precision of laboratory analyses. Those replicates with an RPD greater than 20% were examined more closely and those results that professional judgment determines to be affected are qualified

Laboratory replicates where both values are less than the reporting limit and their difference is less than the reporting limit are not qualified. There were a number of such cases because the laboratories estimated the concentrations down to their MDL.

All laboratory replicates were within the project specifications.

4.4 Matrix Spikes

Matrix Spike and Matrix Spike Duplicate (MS/MSD) percent recoveries were evaluated to determine acceptable accuracy based on method-specific percent recoveries. Precision was evaluated by calculating the RPD of the MS/MSD recovery results. When spikes are reported below the accepted range they indicate a low bias to the results and when reported above the accepted range they indicate a high bias.

QA/QC guidelines indicate that no action need be taken on MS/MSD data alone. The data reviewer may use the MS/MSD results in conjunction with other QC criteria when determining the need for further qualification. The Matrix Spike and their duplicates were recovered within an acceptable range during the project year with the following exceptions.

All Matrix Spike/Matrix Spike Duplicates were recovered within the proper range.

4.5 Laboratory Control Samples

Laboratory Control Spikes and their duplicates (LCS/LCSD) are solutions of known compounds and selected concentrations in clean laboratory water. Precision and accuracy are evaluated in a similar fashion as MS/MSDs with the exception that there is no source sample to subtract and no matrix interference issues.

All Laboratory Control Spikes were recovered within the proper ranges.

4.6 Standard Reference Material

Standard Reference Material (SRM) is analyzed to evaluate accuracy. The data quality objectives were met in all cases.

4.7 Total and Dissolved Metals

Total and dissolved metal pairs were examined for cases where the dissolved fraction was substantially higher than the total fraction. In the few cases where this occurred the relative percent difference was small or the absolute difference was less than the reporting limit with one exception. Dissolved zinc was 11 ug/L for the asphalt lysimeter for the sixth storm event (7 Dec 2007) and total zinc was reported at 9 ppb with a 1 ug/L reporting limit. The dissolved zinc for this station event was qualified with a “J” to indicate it should be considered an estimate. The total zinc was already qualified as an estimate due to a blank hit.

Kinnetic Laboratories, Inc. 2005b. Sampling and Analysis Plan for the County of San Diego Department of General Services, Model Municipal Operations Center, Porous Pavement Water Quality Monitoring Program, Grant Agreement No. 03-264-559-0

Kinnetic Laboratories, Inc. 2005. City of Long Beach Stormwater Monitoring Report, 2004/2005.

Kinnetic Laboratories, Inc. 2005a. Quality Assurance Project Plan, County of San Diego Model Municipal Operations Center, Porous Pavement Water Quality Monitoring Program. Grant Agreement Number: 03-264-559-0

Kinnetic Laboratories, Inc. 2007. Quality Assurance Project Plan and Monitoring Plan, County of San Diego Model Municipal Operations Center – Phase II, Porous Pavement Water Quality Monitoring Program. Grant Agreement Number: 06-135-559-0

MEC-Weston. 2004. Quality Assurance Project Plan, County of San Diego Model Municipal Operations Center Treatment Train Water Quality Monitoring Program. Grant Agreement Number: 03-264-559-0

Table C-1. Relative and Absolute Differences for Field Duplicate Samples Taken at the County Operations Center During the Phase II Studies.

	20-Feb-07 Reference		21-Apr-07 MSF-Out		7-Dec-07 Reference		5-Jan-08 Reference		23-Jan-08 MFS3-In	
CONSTITUENT	RPD	Abs Diff	RPD	Abs Diff	RPD	Abs Diff	RPD	Abs Diff	RPD	Abs Diff
Hardness (mg/L)	6	0.4	4	1	0	0	6	1	8	0.60
SSC (mg/L)	10	1.3	1	0.2	21	39	20	10	3	4
>63 microns	20	0.49	28	0.37	54	13	14	0.83	20	6
<63 microns	1	0.2	4	0.6	31	52	24	11	2	2
TSS (mg/L)	4	1	6	1	11	20	17	9	0	0
COD (mg/L)	4	1	5	4	14	6	5	2	15	8
DOC (mg/L)	4	0.2	0	0	2	0.2	15	0.90	4	0.10
Total P	13	0.013	12	0.03	0	0	7	0.01	22	0.03
Ortho-P (mg/L)	7	0.003	0	0	0	0	4	0.00	8	0.00
Ammonia-N (mg/L)	0	0	10	0.06	7	0.02	21	0.03	11	0.02
TKN (mg/L)	35	0.39	6	0.1	8	0.1	2	0.01	23	0.15
Nitrate-N (mg/L)	4	0.01	0	0	0	0	0	0	0	0
Total Cadmium (ug/L)	0	0	4	0.02	8	0.03	19	0.01	4	0.01
Diss. Cadmium (ug/L)	0	0	6	0.02	8	0.01	42	0.01	4	0.00
Total Copper (ug/L)	13	1.2	0	0	3	1	10	1	3	1
Diss. Copper (ug/L)	2	0.1	3	1	2	0.20	2	0.10	2	0.10
Total Lead (ug/L)	10	2	0	0	0	0	8	0.30	0	0
Diss. Lead (ug/L)	0	0	0	0	4	0.10	23	0.10	7	0.10
Total Zinc (ug/L)	3	2	0	0	0	0	12	30	0	0
Diss. Zinc (ug/L)	6	2	4	10	7	10	8	4	0	0
Calculated Values ¹										
Oil&Grease _(COD) (mg/L)	1	0.04	2	5	4	0.20	0	0	5	0.30
Oil&Grease _(DOC) (mg/L)	3	0.06	0	0	4	0.10	11	0.20	3	0.03

1. Kayhanian, M, S. Khan, and M.K. Stenstrom. 2004. A new method to estimate oil and grease event mean concentration in highway runoff. StormCon 2004.

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